[19] 中华人民共和国国家知识产权局

[51] Int. Cl[7]
C09C 3/00

[12] 发明专利说明书

[21] ZL 专利号 01108083.3

[45] 授权公告日 2004 年 10 月 6 日

[11] 授权公告号 CN 1169883C

[22] 申请日 2001.2.7 [21] 申请号 01108083.3
[71] 专利权人 南京大学
地址 210093 江苏省南京市汉口路 22 号
[72] 发明人 周全法 徐 正 包建春
审查员 殷朝晖

[74] 专利代理机构 南京知识律师事务所
代理人 黄嘉栋
权利要求书 1 页 说明书 3 页

[54] 发明名称 纳米级氧化银及其生产工艺

[57] 摘要

一种纳米级氧化银，其平均粒径为 80－100nm，最大粒径与最小粒径之差≤5nm。其制法是将硝酸银加水溶解，在搅拌下逐渐加入浓氨水，配成银氨溶液。另将固体氢氧化钠和保护剂加水搅拌溶解，配成碱溶液。保护剂可以是聚乙烯吡咯烷酮或聚乙烯醇。将银氨溶液在搅拌下逐渐加入到碱溶液中，再充分搅拌后，离心过滤出氧化银，经洗涤和真空干燥后，即得稳定性和分散性好、粒度分布均匀的纳米级氧化银。该方法可用于工业化生产。

[19] Intellectual Property Bureau of the Peoples' Republic of China

[51] Int. Cl[7]
C09C 3/00

[12] Novel Application Patent Public Announcement

[21] Application No.0118083.3

[43] Announcement Date: October 6, 2004

[11] Announcement No. CN 1169883C

---

[21] Application No.: 01108083.3

[22] Date of Application: February 7, 2001

[71] Assignee: University of Nanjing

Address: No. 22, Han Kou Road

Nanjing, Jiangsu Province, People's Republic of China 210093

[72] Inventors: ZHOU Quan-fa, XU Zheng, and BAO Jian-chun

Examiner: YIN Chao-hui

[74] Patent Representative Agency: Nanjing Zhi Shi (Knowledge) Law Office

Representative: Huang Jia-dong

Patent Claims 1 page; Descriptions 3 pages

---

[54] Name of Invention: Nanometer Grade Silver Oxide and the Process for Its Manufacturing

[57] Summary

A nanometer grade silver oxide; the average particle size of which is 80 – 100 nm; the difference between the largest particle size and the smallest particle size is $\leq$ 5 nm. The process of preparation is to dissolve silver nitrate in water, gradually adding concentrated ammonia water while stirring, to obtain an ammoniacal silver solution. Solid sodium hydroxide and a protective agent are then dissolved separately in water while stirring, to obtain an alkali solution. The protective agent may be polyvinyl-pyrrolidone or polyvinyl alcohol. The ammoniacal silver solution is gradually added to the alkali solution while stirring; after further through stirring, the solution is centrifuged to separate the silver oxide precipitate, which is then washed and vacuum dried; obtaining a nanometer grade silver oxide, with good stability and dispersibility, as well as uniformly distributed particle size. The process may be used for industrial manufacturing.

Published by Intellectual Property Publisher

ISSN 1008 – 4274

Patent Claims

1. A nanometer grade silver oxide, the characteristics of which are that the average particle size is 80 – 100 mm; the difference between the largest particle size and the smallest particle size is $\leq$ 5 nm.

2. A process for manufacturing the nanometer grade silver oxide as mentioned in Claim 1, the characteristic of which are that an aqueous solution of silver nitrate is prepared, followed by the addition of ammonia water to obtain a ammoniacal silver solution, which is then gradually added to a sodium hydroxide solution with pre-added protective agent, forming super fine silver oxide precipitates; after filtration, washing, and drying, super fine silver oxide with an average particle size of 80 – 100 nm is obtained; the difference between the largest particle size and the smallest particle size is $\leq$ 5 nm; the protective agent mentioned is polyvinyl-pyrrolidone or polyvinyl alcohol.

Descriptions

Nanometer Grade Silver Oxide and the Process for Its Preparation

This invention is pertaining to nanometer grade silver oxide and the process for its preparation.

Silver oxide (Ag_2O) has been widely used in the industry for electronic components, button batteries, preservatives or antiseptics, cleaning agents, glass coloring agent and polishing agent, as well as chemical catalysts, etc.. Thirty percent of industrial silver usage is for production of silver oxide (or silver nitrate), in which the silver oxide consumption by the electronic component industry accounts for 90 % of the total silver oxide. Currently, domestic silver oxide are primarily prepared from the reaction of a silver nitrate solution with a sodium hydroxide solution to obtain a silver oxide precipitate, which is then washed, separated, and dried to obtain the silver oxide finish product. The major technical indexes (indicators) of the product include silver oxide content, clarity test and nitric acid insoluble materials, free alkali, nitrate salts, hydrochloric acid un-precipitated material content, and drying weight loss, etc..

The major existing issues include:

1. There is no particle size index in current product; the particle size is difficult to meet the requirements of various industries. The silver oxide used in the electronic component industry is usually prepared into a silver oxide paste, which requires extended ball milling levigation to reduce the size (require approximately 7 days) before mixing with other materials, which is then printed onto a device substrate (chip) through silk screening. The particle size of silver oxide is directly impacting the quality of the prepared silver paste and the cost of silk screen, which is in turn affecting the quality of the device. The requirement of the silver oxide particle size for the electronic industry is "the smaller the better". Current manufacturing technologies used both domestically and abroad are difficult to meet these requirements. Silver oxide used in the industries for chemical catalyst, medical antiseptics, glass coloring, etc., also requires a particle size of "the smaller the better".

2. Although domestically produced silver oxide is meeting the national purity standard, however, due to current processing technology, the particle size of current product is too large, making it easy to enclose impurities; it is very difficult to obtain high or super high purity grade silver oxide.

The objective of this invention is to provide a nanometer grade silver oxide, with good stability and dispersibility, and a uniformly distributed particle size, as well as a process for industrial manufacturing.

Technical thinking behind this invention: When a silver nitrate solution is reacting with a sodium hydroxide solution, the Ag^+ ion concentration in the solution is usually too high, the rate of growth of the silver oxide particle produced in the reaction system is too fast; at the same time, it is very easy to form aggregates between the particles, as a result, the particle size of the silver oxide produced is too large. If the Ag^+ ion concentration can be reduced during reaction, allowing the formation of silver oxide to speed up while the growth rate to slow down; at the same time, if the silver oxide particles are protected once they are formed, to prevent aggregate from forming, then, a silver oxide product with very small particle size can be prepared.

Therefore, the technical schemes of this invention are as follows:

A nanometer grade silver oxide, with an average particle size of ≤100 nm; the difference between the largest particle size and the smallest particle size is ≤ 5 nm.

A process for manufacturing the nanometer grade silver oxide, which involves the preparation of an aqueous solution of silver nitrate, concentrated ammonia water is added to obtain an ammoniacal silver solution, which is then gradually added to a sodium hydroxide solution with pre-added protective agent, forming super fine silver oxide precipitates; after filtration, washing, and drying, super fine silver oxide with an average particle size of 80 – 100 nm is obtained;

the protective agent mentioned above may be polyvinyl-pyrrolidone or polyvinyl alcohol.

The specific process involves:

Dissolve 50 – 100 (parts by weight, same hereafter) of silver nitrate in 300 parts of water, add 100 – 400 parts of concentrated ammonia water gradually while stirring to obtain an ammoniacal silver solution. Separately, 500 parts of water is added to 20 – 40 parts of solid sodium hydroxide and 0.2 – 1.0 parts of protective agent; it is stirred until dissolved to obtain an alkali solution. The protective agent may either be polyvinyl-pyrrolidone or polyvinyl alcohol. The ammoniacal silver solution mentioned above is gradually added to the alkali solution mentioned above while stirring. After the solution is further thoroughly stirred for 4 – 8 hours, the silver oxide precipitate is separated through centrifugation; the silver oxide is then washed with water for 3 times, followed by washing with ethanol for 3 times, and is dried under vacuum at a temperature below 80°C, to obtain a nanometer grade silver oxide. The nanometer grade silver oxide prepared by the method of this invention has a particle size of 80 – 100 nm, has good stability and dispersibility, with a uniform particle size distribution.

Using the manufacturing process of this invention, the silver oxide obtained has an average particle size of less than 100 nm, the difference between the largest particle size and the smallest particle size is ≤ 5 nm; since a protective agent is being used, it has very good stability and dispersibility.

Application Example 1

Dissolve 50 Kg of silver nitrate in 300 L of water, add 100 L of concentrated ammonia water gradually while stirring to obtain an ammoniacal silver solution. Separately, 500 L of water is added to 40 Kg of solid sodium hydroxide and 0.2 Kg of protective agent (polyvinyl-pyrrolidone, or PVP, molecular weight 30,000); it is stirred until dissolved to obtain an alkali solution. The ammoniacal silver solution is gradually added to the alkali solution while stirring. After the solution is further thoroughly stirred for 4 hours, the silver oxide precipitate is separated through centrifugation; the silver oxide is then washed with water for 3 times, followed by washing with ethanol for 3 times, and is dried under vacuum at a temperature below 80°C, to obtain a nanometer grade silver oxide. The nanometer grade silver oxide prepared in this application example has an average particle size of 88 nm; the difference between the largest particle size and the smallest particle size is ≤ 5 nm.

Application Example 2

Dissolve 100 Kg of silver nitrate in 300 L of water, add 100 L of concentrated ammonia water gradually while stirring to obtain an ammoniacal silver solution. Separately, 500 L of water id added to 25 Kg of solid sodium hydroxide and 1.0 Kg of protective agent (polyvinyl-pyrrolidone, molecular weight 30,000); it is stirred until dissolved to obtain an alkali solution. The ammoniacal silver solution is gradually added to the alkali solution while stirring. After the solution is further thoroughly stirred for 8 hours, the silver oxide precipitate is separated through centrifugation; the silver oxide is then washed with water for 3 times, followed by washing with ethanol for 3 times, and is dried under vacuum at a temperature below 80°C, to obtain a nanometer grade silver oxide. The nanometer grade silver oxide prepared in this application example has an average particle size of 100 nm; the difference between the largest particle size and the smallest particle size is $\leq$ 5 nm.

Application Example 3

Dissolve 100 Kg of silver nitrate in 300 L of water, add 400 L of concentrated ammonia water gradually while stirring to obtain an ammoniacal silver solution. Separately, 500 L of water is added to 40 Kg of solid sodium hydroxide and 1.0 Kg of protective agent (polyvinyl-pyrrolidone, molecular weight 30,000); it is stirred until dissolved to obtain an alkali solution. The ammoniacal silver solution is gradually added to the alkali solution while stirring. After the solution is further thoroughly stirred for 8 hours, the silver oxide precipitate is separated through centrifugation; the silver oxide is then washed with water for 3 times, followed by washing with ethanol for 3 times, and is dried under vacuum at a temperature below 80°C, to obtain a nanometer grade silver oxide. The nanometer grade silver oxide prepared in this application example has an average particle size of 82 nm; the difference between the largest particle size and the smallest particle size is $\leq$ 5 nm.

Application Example 4

Dissolve 50 Kg of silver nitrate in 300 L of water, add 400 L of concentrated ammonia water gradually while stirring to obtain an ammoniacal silver solution. Separately, 500 L of water is added to 40 Kg of solid sodium hydroxide and 1.0 Kg of protective agent (polyvinyl-pyrrolidone, molecular weight 30,000); it is stirred until dissolved to obtain an alkali solution. The ammoniacal silver solution is gradually added to the alkali solution while stirring. After the solution is further thoroughly stirred for 8 hours, the silver oxide precipitate is separated through centrifugation; the silver oxide is then washed with water for 3 times, followed by washing with ethanol for 3 times, and is dried under vacuum at a temperature below 80°C, to obtain a nanometer grade silver oxide. The nanometer grade silver oxide prepared in this application example has an average particle size of 80 nm; the difference between the largest particle size and the smallest particle size is $\leq$ 5 nm.

Application Example 5

Dissolve 50 Kg of silver nitrate in 300 L of water, add 100 L of concentrated ammonia water gradually while stirring to obtain an ammoniacal silver solution. Separately, 500 L of water is added to 15 Kg of solid sodium hydroxide and 0.2 Kg of protective agent (polyvinyl-pyrrolidone, or PVP, molecular weight 30,000); it is stirred until dissolved to obtain an alkali solution. The ammoniacal silver solution is gradually added to the alkali solution while stirring. After the solution is further thoroughly stirred for 8 hours, the silver oxide precipitate is separated through centrifugation; the silver oxide is then washed with water for 3 times, followed by washing with ethanol for 3 times, and is dried under vacuum at a temperature below 80°C, to obtain a nanometer grade silver oxide. The nanometer grade silver oxide prepared in this application example has an average particle size of 92 nm; the difference between the largest particle size and the smallest particle size is $\leq$ 5 nm.